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TECHNICAL REPORT ARLCD-TR-80002

TRIAMINOGUANIDINIUM ION IN TRIAMINOGUANIDINIUM NITRATE BY THE MINDO/3 SEMI-EMPIRICAL SCF-MO TREATMENT

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JUNE 1980

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DOVER, NEW JERSEY

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SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER ARLCD-TR-80002	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Triaminoguanidinium Ion In Triaminoguanidinium Nitrate by the MINDO/3 Semi-Empirical SCF-MO Treatment		5. TYPE OF REPORT & PERIOD COVERED Final 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Arthur J. Bracuti Yvon P. Carignan		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS ARRADCOM, LCWSL Applied Sciencies Div (DRDAR-LCA-G) Dover, NJ 07801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS ARRADCOM, TSD STINFO (DRDAR-TSS) Dover, NJ 07801		12. REPORT DATE June 1980 13. NUMBER OF PAGES 11
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Triaminoguanidinium nitrate
MINDO/3
Total energy calculations
Cation configuration

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

MINDO/3 semi-empirical SCF-MO calculations on the triaminoguanidinium ion of triaminoguanidinium nitrate have provided information on the total energy, core-core repulsion energy, electronic energy, charge distribution, heat of formation, ionization potential, and dipole moment of the cation. The effect of rotation across the N-N bonds on the values of these parameters is presented. The configuration of the cation with the lowest total energy corresponds to the configuration determined by x-ray analysis on a crystal of triaminoguani-

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dinium nitrate and the energy barrier for the rotation of the three primary amino groups is of the order of 1.38 eV (31.8 Kcal).

ACKNOWLEDGMENT

The authors are grateful to Dr. T. Vladimiroff, of the Applied Sciences Division, LCWSL, ARRADCOM, for stimulating discussions.

TABLE OF CONTENTS

TABLES

FIGURES

INTRODUCTION

Triaminoguanidinium nitrate ($TAG.NO_3$) should offer more than a passing interest on the basis of its nitrogen content alone. Compared to ammonium nitrate (35.0%N) or guanidinium nitrate (45.9%N), triaminoguanidinium nitrate contains 58.7% total nitrogen. In spite of this attractive feature, the interest in $TAG.NO_3$ has been limited so far mainly to its possible application in propellants technology.

The structure of this salt was recently established by x-ray diffractometry (ref 1) which revealed the fact that the carbon atom, three hydrogen atoms, and the six nitrogen atoms of the triaminoguanidinium (TAG+) ion lie in a mirror plane, while the primary amino hydrogens are reflected below and above this plane. A representation of the TAG+ ion structure found in the crystal of triaminoguanidinium nitrate is shown in figure 1.

Why the TAG+ ion in the crystal adopts this configuration in preference to others obtainable by simple rotation across the N-N bonds is a challenging question. Are the factors which determine this preference dictated mainly by the crystalline forces or by the directional forces associated with hydrogen bonds? Or is the configuration of figure 1 preferred over others (the 180° rotation across the N-N bonds shown in figure 2, for example) simply because of its lower total energy content? Basically, these questions relate to the charge distribution in the cation which, in turn, sets the magnitude of the energy barrier to rotation across the N-N bonds.

Considerations of this nature directs attention to the semi-empirical SCF-MO treatment, MINDO/3, which has been established (ref 2) as reliable in calculating energy, charge distribution, and other properties for the ground state of a large variety of molecular species. By means of MINDO/3 calculations (ref 3), the following treatment addresses the magnitude of the effect produced by the rotation across the three N-N bonds on the total energy of the cation. Since MINDO/3 can provide pertinent data on other properties for the ground state of the cation, these are also included in the results.

RESULTS

The input bond lengths and angles used for the MINDO/3 calculations are those obtained by the x-ray study (ref 1), including the corrections for thermal motion of the atoms assumed to be moving independently. To keep the optimized molecular geometry calculated by MINDO/3 as close as possible to the experimental x-ray geometry (fig. 1), a single optimization parameter was requested from the molecular geometry optimization program; specifically, the 120° N-C-N angle measured by x-ray. The calculated optimized geometry expanded this angle to 120.4° and values of charge distribution, electron density distribution, heat of formation (kcal/mole), ionization potential (eV), electronic energy (eV), core-core repulsion energy (eV), total energy (eV), and dipole moment (Debye) were obtained. Since the optimized geometry differs so slightly from the experimental (only of 0.4° in one angle while bond lengths and other angles are the same), it is reasonable to assign calculated values to the actual molecular geometry of the TAG+ ion in the crystal. Five other sets of data were obtained by rotating the primary amino hydrogens from their actual positions in the crystal structure (table 1). Because the H-N-H angles for the three sets of amino hydrogens are quite different (96.98°, 105.26°, 122.56°), the rotation performed with these hydrogens differs with their location in the cation.

The effect of the rotation operations on the calculated molecular parameters is shown in table 2. The variation of the total energy as a function of the rotation sequence is plotted in figure 3.

DISCUSSION

Within the constraints imposed on the TAG+ ion structure, which limits the energy optimization process to seeking its minimum through variation of a single angle, the core-core repulsion energy is lowest for the configuration corresponding to that observed from the x-ray analysis, (0° rotation, fig. 1). With rotation, this repulsion energy increases to a maximum (gain of 90 eV) at 180° rotation, corresponding to the configuration shown in figure 2. By contrast, the electronic energy decreases with rotation, reaching its minimum value at the 180° rotation angle. The net result, however, is that the total energy (the sum of core-core repulsion energy and electronic energy) for the ground state of the TAG+ ion is lower for configuration 1 (0° rotation) than for any other configuration obtained through rotation of the primary amino hydrogens (fig. 3). The energy barrier to rotation for all three sets of amino hydrogens is calculated to be 1.38 eV (31.8 Kcal) or 10.6

Kcal per NH_2 group. According to the MINDO/3 calculations, the configuration adopted by the TAG+ ion in the crystal of triaminoguandinium nitrate is anticipated on the basis of minimum energy criteria for stability.

Relaxing the constraints in the optimization process does not invalidate this result. Instead of optimizing a single angle in the structure, for example, if two bond lengths, one bond angle and three twist angles are optimized simultaneously, the energy yielded will be lower by approximately 23 Kcal for the x-ray structure (configuration 1) than for any other configuration.

CONCLUSIONS

According to the MINDO/3 calculations, which treat the TAG+ ion as if it were isolated in space and thus subjected to no external force, the lowest energy configuration for this cation corresponds to that in the crystal of triaminoguandinium nitrate where external forces are known to operate. The combination of the different forces or dynamic effects in the crystal, only serve to produce local perturbations within the cation, resulting in deviations from the expected C_{3h} symmetry. One interesting general conclusion which could be drawn from this work is that the triaminoguanidinium ion, irrespective of the nature of the anion, would adopt the configuration observed in the nitrate salt simply because of its inherently lower total energy content.

REFERENCES

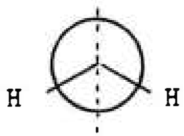
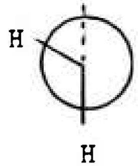
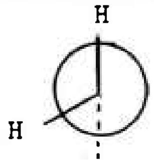
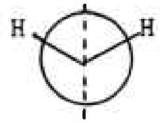
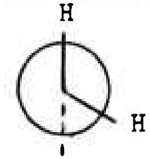
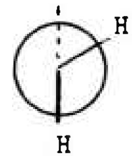
1. A. J. Bracuti, Acta Cryst., Vol B35, pp 760-761 (1979)

2. R. C. Bingham, M. J. S. Dewar, and D. H. Le, J. Am. Chem. Soc., Vol 97, p 1285 (1975)

3. Ibid, p 1294 (1975)

4. Calculations conducted on a CDC 6600 computer using the molecular geometry optimization program of M. J. S. Dewar, et al, QCPE No. 279, Indiana University, Bloomington, Indiana, April 1973,

Table 1. Sequence of rotations of the primary amino hydrogens in the triaminoguanidinium ion

Position of hydrogen atoms[1]	Sequence and Angles of Rotations[2,3] a[4]	b	c	d	e	f
						
4 & 5	0^{o}	48.49^{o}	83.02^{o}	48.49^{o}	48.49^{o}	83.02^{o}
8 & 9	0^{o}	52.63^{o}	74.74^{o}	52.63^{o}	52.63^{o}	74.74^{o}
12 & 13	0^{o}	61.28^{o}	57.44^{o}	61.28^{o}	61.28^{o}	57.44^{o}

[1] Refers to numbering in figure 1.

[2] Rotation clockwise looking along the N-N bond in the direction of the hydrogen atoms.

[3] The dotted lines through the circles refer to the plane of symmetry of the cation.

[4] Corresponds to configuration 1, figure 1.

Table 2. Effect of rotation of the primary amino hydrogens on molecular parameter (MINDO/3 calculations)

Rotation*	Heat of formation (Kcal/mole)	Ionization potential (eV)	Electronic energy (eV)	Core core repulsion energy (eV)	Total energy (eV)	Dipole moment (deby)
a	236.81	14.274	-5953.875	+4549.925	-1403.951	0.0671
b	243.84	13.447	-5975.041	+4571.395	-1403.646	4.1406
c	268.595	13.531	-6033.434	+4630.861	-1402.573	4.2580
d	262.574	14.452	-6043.073	+4640.239	-1402.833	0.2801
e	268.595	13.521	-6033.434	+4630.861	-1402.572	4.2583
f	243.837	13.447	-5975.041	+4571.395	-1403.646	4.1406

*Letters a through f refer to the rotation angles given in table 1.

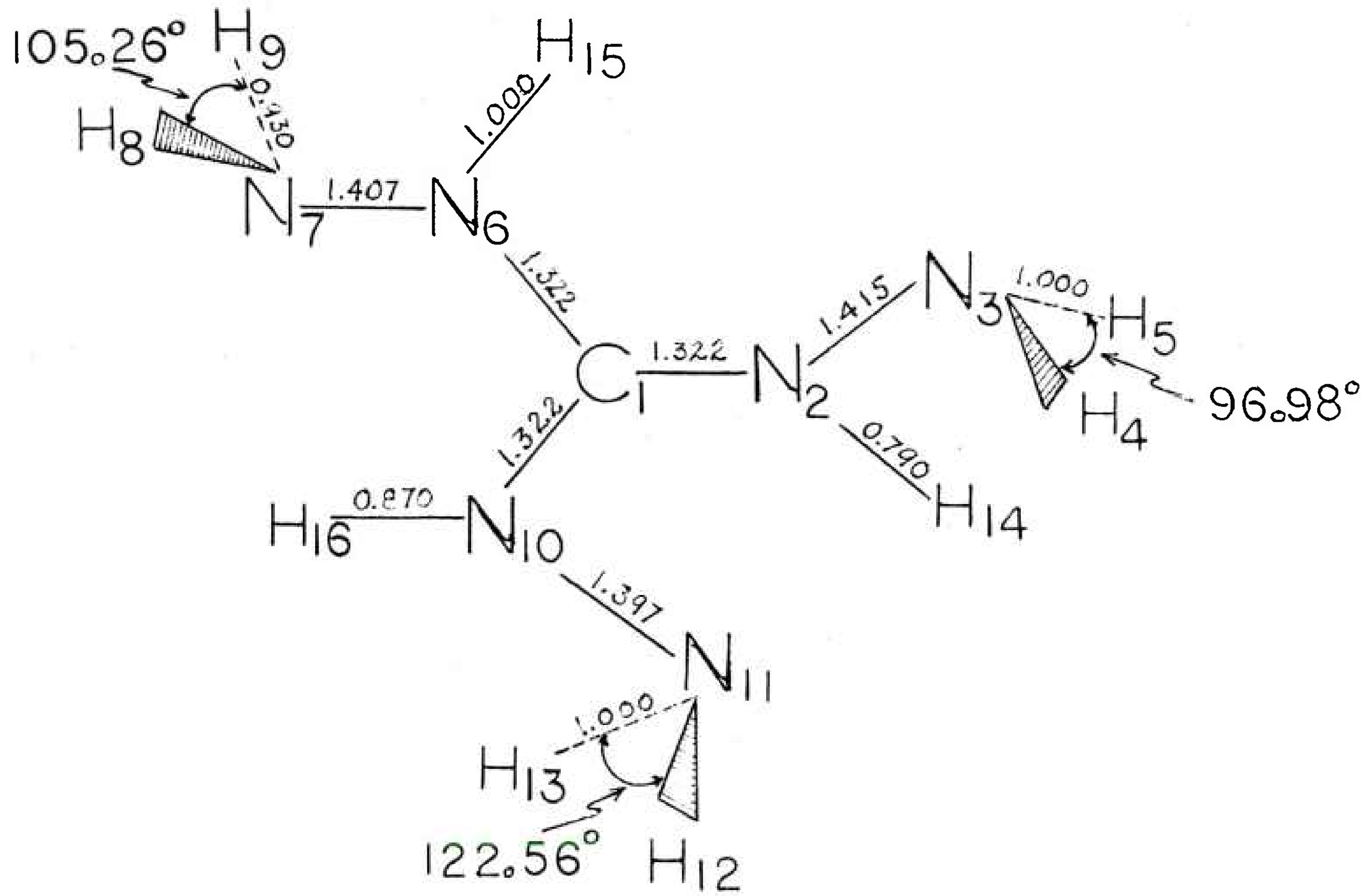


Figure 1. Molecular configuration 1 and bond lengths for the triaminoguanidinium ion in the crystal of triaminoguanidinium nitrate.

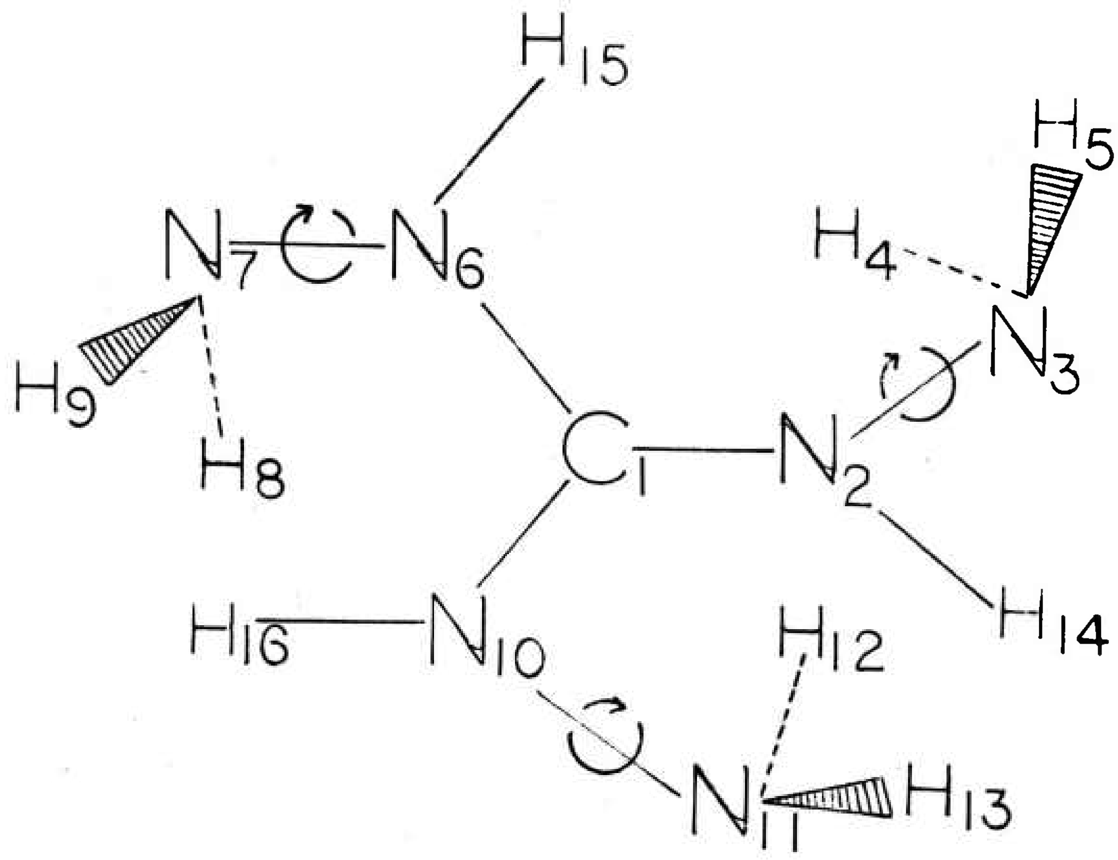


Figure 2. Molecular configuration 2 of the triaminoguanidinium ion after rotation of the N-N bonds by 180°.

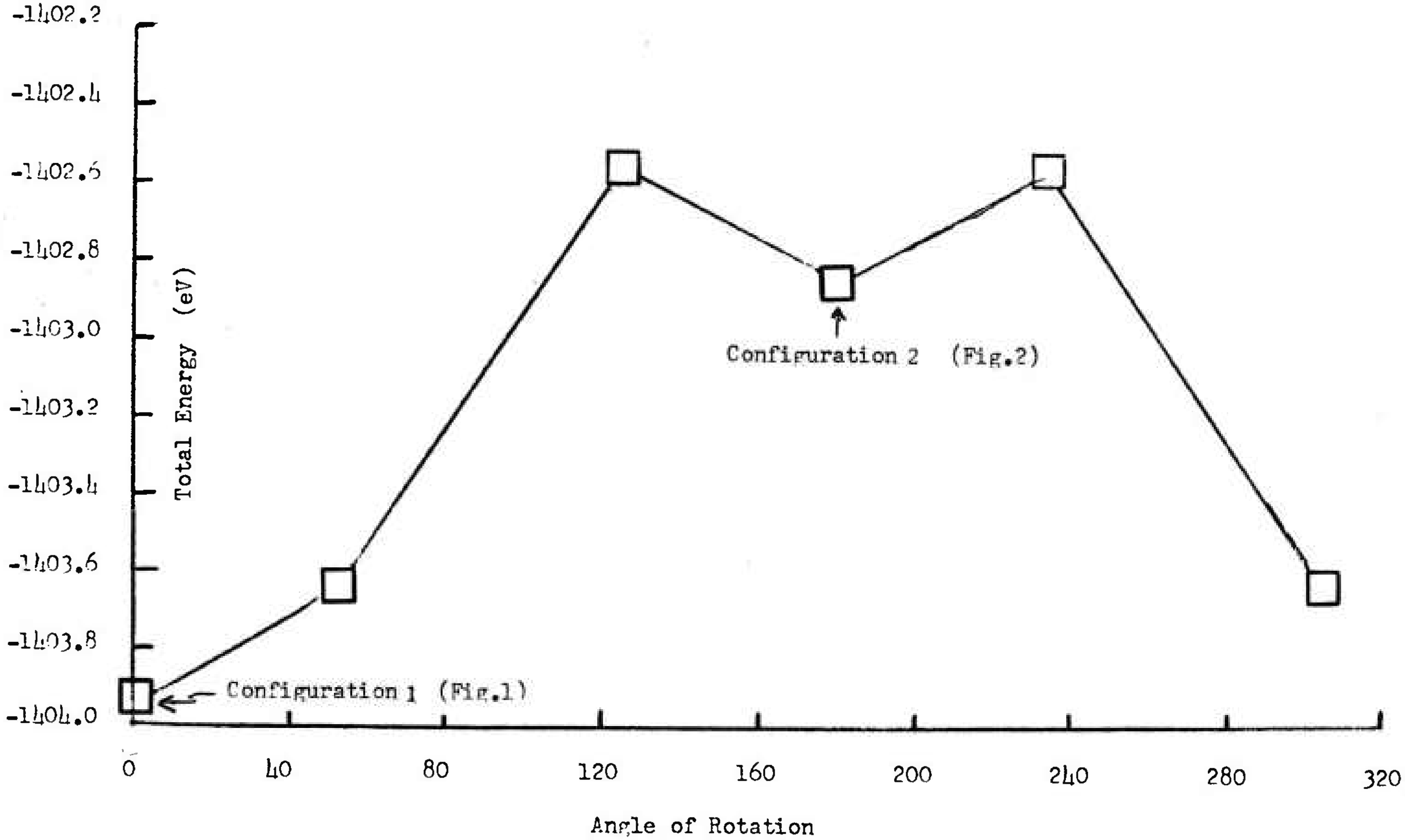


Figure 3. Variation of total energy of triaminoguanidinium ion with the angles of rotation.

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